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IMPROVEMENTS IN THE PREPARATION OF  
CERTAIN DYESTUFF INTERMEDIATES

BY

JOHN WESLEY BIRCHARD

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THESIS

FOR THE

DEGREE OF BACHELOR OF SCIENCE

IN

CHEMICAL ENGINEERING

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COLLEGE OF LIBERAL ARTS AND SCIENCES

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THIS IS TO CERTIFY THAT THE THESIS PREPARED UNDER MY SUPERVISION BY

..... John Wesley Birchard .....

ENTITLED..... Improvements in the Preparation of Certain Dye stuff .....

..... Intermediates .....

IS APPROVED BY ME AS FULFILLING THIS PART OF THE REQUIREMENTS FOR THE

DEGREE OF..... Bachelor of Science in Chemical Engineering .....

..... Oliver Kamm .....

Instructor in Charge

APPROVED:.....


W. A. Hayes

HEAD OF DEPARTMENT OF.....

Chemistry

210738

266 D 18 Robinson



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## IMPROVEMENTS IN THE PREPARATION OF CERTAIN DYESTUFF INTER - MEDIATES.

### General Introduction.

It is not generally known that even before the war ten per-  
cent of all the dyestuffs used in the United States were made in  
this country <sup>1</sup>. The intermediate coal tar products that were re-  
quired for the manufacture were, however, usually imported from  
Europe, and this will explain why, with the cutting off of foreign  
supplies, American manufacturers experienced their chief difficult-  
ies not in the preparation of the dyes themselves but more often in  
the manufacture of intermediates. After pure intermediates were  
placed on the market no difficulties were found in preparing the  
well known colors required by the textile industry. The present  
work was undertaken in order to investigate the preparation of  
some of these intermediate products the production of which has  
been known to offer some difficulties in technical manufacture.



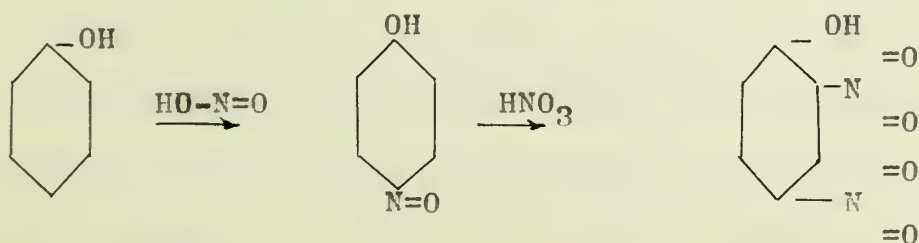
Part I. Preparation of p-nitrosophenol and a Study of its Oxidation with Nitric Acid.

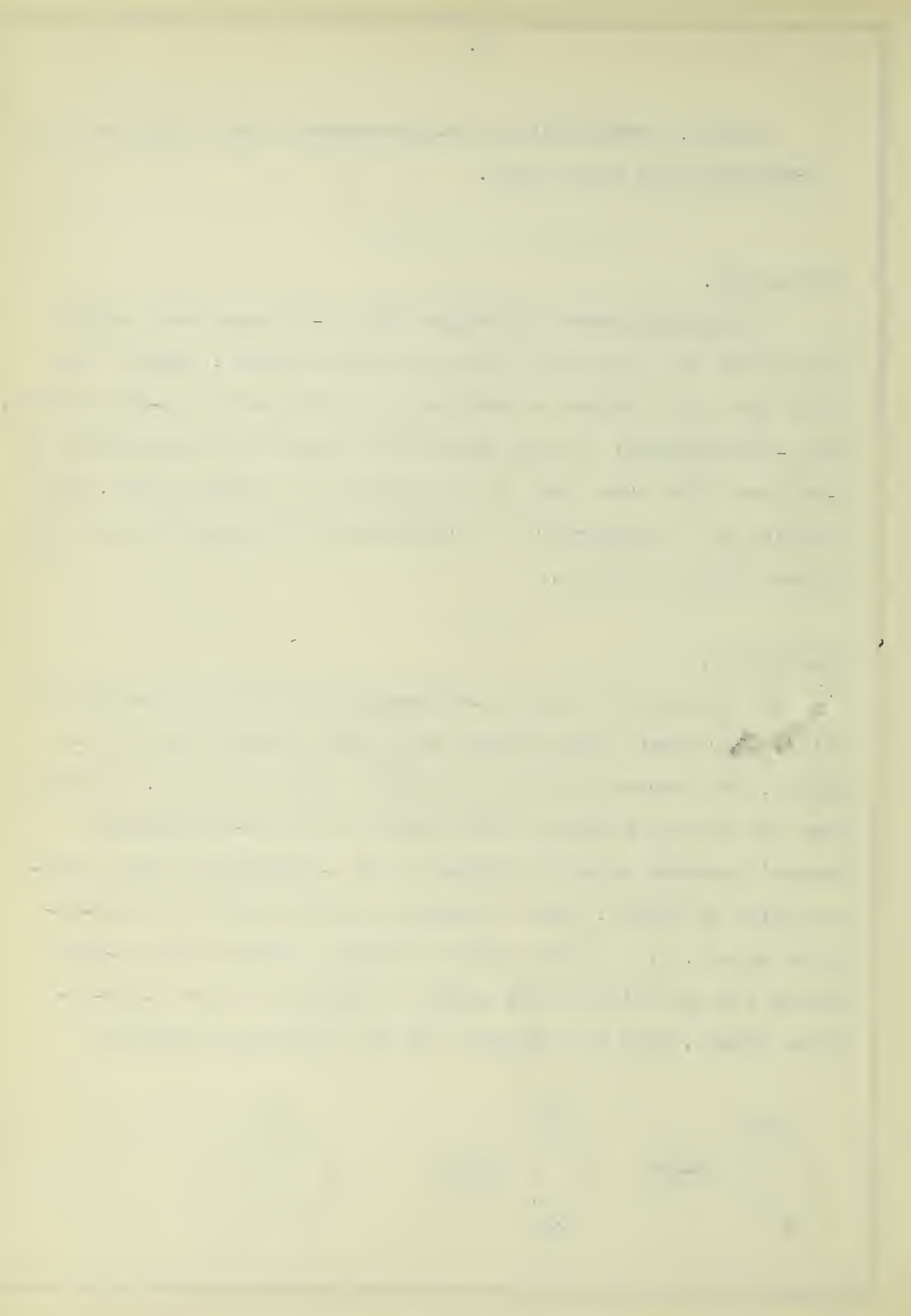
Historical.

It has been shown by Bridge<sup>2</sup> that p-nitrosophenol can be prepared by the action of nitrous acid upon phenol. Baeyer<sup>3</sup> contends that this product is oxidized by nitric acid to p-nitrophenol. The p-nitrosophenol is also produced by action of hydroxylamine on p-quinone which shows that it can behave as a quinone oxime. This accounts for its behavior as a chromophore in dyestuffs since the quinone ring is present.

Theoretical.

The aim was to prepare p-nitrosophenol starting according to Bridge and to make improvements as to the yield and use of reagents. The percent yield was increased from 70% to 95%. The next step was that of oxidation with nitric acid to p-nitrophenol. Baeyer's product which he claimed to be p-nitrophenol had a melting point of 114° C. This is also the melting point of 1,2,4-dinitrophenol. It is shown that the product formed is not p-nitrophenol but that nitric acid causes a nitration to the 1,2,4-dinitrophenol. This is indicated by the following equations:







### Experimental.

A mixture of 82c.c. concentrated  $\text{H}_2\text{SO}_4$  and 400 c.c. water was added gradually to a cold mixture of 60 gms. phenol, 27 gms. NaOH and 54 gms.  $\text{NaNO}_2$  in 1500 c.c. water. The temperature was maintained at  $70^\circ$  C. throughout the experiment. As the  $\text{H}_2\text{SO}_4$  was added slowly a very light yellow color appeared. After more acid had been added a dark brown precipitate was formed. A yield of 70% of p- nitrosophenol was obtained. From a second run made the same way a yield of 57 gms. was obtained whereas the theoretical yield is 78.7 gms.

It was next decided to omit the NaOH since the product was formed in acid solution. Three runs were made with this omission with a yield of about 43 gms. each. The melting point of the product was found to be  $125^\circ$ - $126^\circ$  C. The aim, as stated before, consisted in increasing the yield. In the runs made up to this time a very large dilution had been used so that probably as much as 25% of the p-nitrosophenol formed was dissolved by the water since it is soluble to an appreciable extent. The investigation to increase the yield was made by using a more concentrated solution. The next run consisted of 60 gms. phenol as before but only one half the amount of water used for solution. When the sulphuric acid was first dropped into the mixture of phenol and  $\text{NaNO}_2$  in concentrated solution, a yellow coloration seemed to indicate that the reaction would go on as well in this way as in a high dilution. Upon adding more of the  $\text{H}_2\text{SO}_4$ , the precipitate became very dark and finally black and oily. Upon stirring for about an hour with a mechanical stirrer, the product remained dark and upon





filtering and allowing to stand for a short time a very dark product was formed. The p-nitrosophenol was too impure to be used in subsequent work.

The next investigation was that of using the filtrates over, since they probably contained 25% of the product lost due to solubility. The first run was made similar to the original ones in large dilution. For the second run about one liter of the filtrate was made alkaline and used for dilution. For the third run one liter of the filtrate from the second run was used for the solution. From the first run a yield of 60 gms. were obtained, 100 gms. from the second, and 127 gms. from the third. As the last two runs were above the theoretical yield, they were examined for impurities and  $\text{Na}_2\text{SO}_4$  was found. After they were purified, the last two runs yielded 70 gms. and 74 gms. respectively. This shows that the filtrate can be used over and the yield increased from 70% to 95%.

While this work was being carried on, oxidation of the p-nitrosophenol was attempted. Baeyer<sup>3</sup> was taken as authority for this preparation but results obtained were contrary to his work. His process was to cover p-nitrosophenol with concentrated  $\text{HNO}_3$  and to cool carefully. Baeyer states that the liquid decomposes with evolution of brown fumes. The mass becomes hard under expulsion of final traces of  $\text{HNO}_3$ ; this colorless paste is reported as pure p-nitrophenol. The product which was obtained by this method was not found to be the same as prepared by Baeyer. It was found impossible to prepare his compound this way. In all cases a product which melted at 113-114° C, the same as the compound prepared by Baeyer, was obtained. At first concentrated  $\text{HNO}_3$  with a very



small amount of p-nitrosophenol was tried. This gave red colored crystals which were recrystallized from water. The product consisted of fine nearly white crystals. About 10 gms. of p-nitrosophenol were used with 20 c.c. of water and 10 c.c. concentrated  $\text{HNO}_3$ . The reaction would not proceed as rapidly in large quantities but had to be heated to start the reaction. After the reaction is once started it will complete itself. From 10 gms. of nitroso compound, 6 gms. of oxidized product were obtained. The following procedure was decided upon as the best: Heat  $\text{HNO}_3$ , which is one part concentrated. to two parts water, to  $40^\circ \text{C}$ . Then add all the p-nitrosophenol which will dissolve. For 10 gms. p-nitrosophenol use about 60 c.c. of solution. Heat then until the reaction starts and allow it to proceed without heating.

A larger run of 20 gms. p- nitrosophenol was then oxidized. A yield of 24 gms. of crude product was obtained while the theoretical yield is 22.6 gms. After recrystallizing a portion from hot water a melting point of  $113^\circ$ - $114^\circ \text{C}$  was found. From 40 gms. of p-nitrosophenol, 48 gms of crude product was obtained and 123 gms. from 80 gms. of the nitroso compound. The last run showed traces of impurities. A test was made to determine whether this product was p-nitrophenol or 1,2,4-dinitrophenol since both have the same melting point. It was decided to make a confirmatory test by making the methyl ether. The methyl ether of p-nitrophenol melts at  $51^\circ \text{C}$ , that of dinitrophenol at  $85^\circ \text{C}$ . The latter ether has not been definitely characterized. About 2 gms. of the nitro compound were dissolved in 20 c.c. dilute alkali and 2 c.c. of dimethyl sulfate were added. By using some known p- nitrophenol a derivative was formed which melted at  $52^\circ$ - $53^\circ \text{C}$ . From the un-





known no derivative was formed. This test proved nothing and the acetyl derivative was made. One gram of the unknown was boiled under reflux with 5 gms. of acetic anhydride and a few drops of concentrated  $H_2SO_4$ . A product was formed upon pouring the mixture into 50 c.c. of water with stirring. This proved to be the dinitrophenol compound because it gave a melting point of  $70^{\circ}$ - $71^{\circ}$  C. which agrees with that of the 1,2,4-dinitro derivative.

For further confirmation of the identity, a combustion for the nitrogen content was made. The compound was recrystallized from water and dried in a vacuum desiccator. Mono nitrophenol contains 10% nitrogen and dinitro-phenol contains 15.2% nitrogen. The amount of nitrogen found was 15.87% which together with its melting point and the method of preparation proves the compound to be 1,2,4-dinitrophenol.

#### Conclusion.

The p-nitrosophenol can be prepared successfully in large quantities by omitting NaOH from the procedure of Bridge. The solution in which the p-nitrosophenol is prepared must be very dilute. Good yields, increases from 70% to 95%, are obtained when the filtrate is used repeatedly. The product p-nitrophenol cannot be prepared by oxidation of the p-nitrosophenol with nitric acid but the 1,2,4-dinitrophenol is readily prepared.



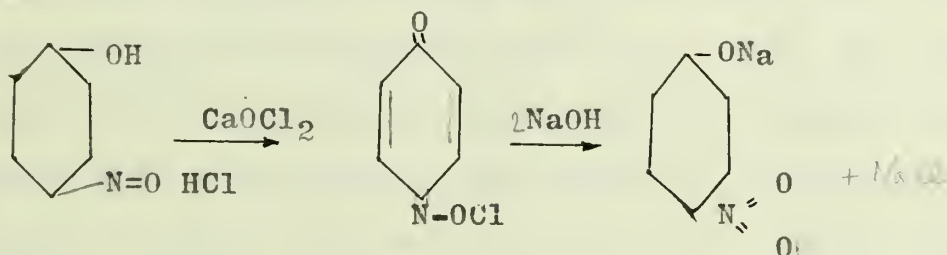
## Part II. Preparation of p-Nitrophenol and Some of its Derivatives.

### Historical.

The preparation of p-nitrophenol has been successfully carried out by several investigators but Baeyer's<sup>3</sup> work was followed mostly. It was undertaken by treatment of p-chloronitrobenzene prepared by Engelhardt<sup>4</sup>. Nitrophenol has not been prepared from this compound. Möhlau<sup>5</sup> was followed for preparation of p-nitrosophenol hydrochlorite and preparation of p-nitrophenol was undertaken from this. The process of Wagner<sup>6</sup> was followed for its preparation from p-nitroacetanilide. The next product, p-nitrophenetol, has been prepared by Weddige<sup>7</sup>.

### Theoretical.

The object in all experiments was to make the sodium salt of p-nitrophenol by the refluxing of some derivative with NaOH. By treating p-nitrosophenol with bleaching powder, p-nitrosophenol hydrochlorite was prepared. The subsequent formation of p-nitrophenol by refluxing with NaOH was tried.

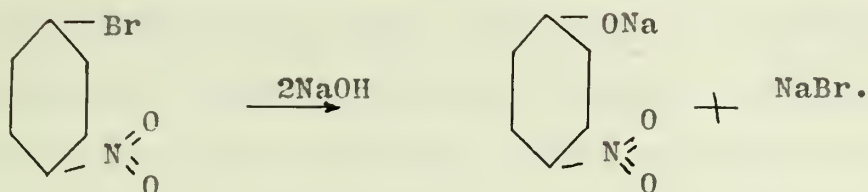


The p-nitrophenol could not be formed this way.

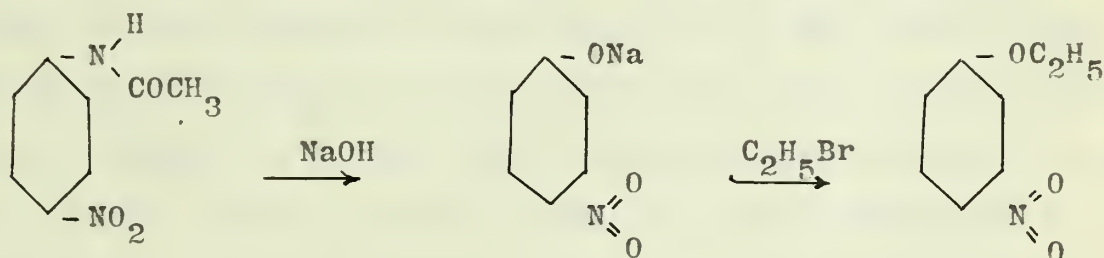




The next reaction to be tried was the formation of p-nitrophenol from p-chloronitrobenzene or p-bromnitrobenzene.



The most successful reaction was the formation of p-nitrophenol from p-nitroacetanilide. This was then carried further to p-nitrophenetol.



#### Experimental.

The directions of Mohlau<sup>4</sup> were followed for the preparation of p-nitrosophenol hydrochlorite. Exactly 10 gms. of p-nitrosophenol were dissolved in 500 gms. water and 5 c.c. HCl (sp.gr.1.185) and a solution of bleaching powder was added. The reaction resulted in the formation of yellow crystals which could not be converted into p-nitrophenol with NaOH but returned to p-nitrosophenol. The next step was the formation of p-nitrophenol by refluxing bromo or chloronitrobenzene with NaOH. The first run was with one gram of the p-bromnitrobenzene under the reflux with



25 c.c. 10% NaOH for one hour. From this trial no p-nitrophenol was obtained. The second run was refluxed for ten hours when a small amount of p-nitrophenol was formed. For the next run p-chloronitrobenzene was used. Three gms. of a solution of 30% NaOH were used for 2 gms. p-chloronitrobenzene. A mixture of 25 gms. p-chloronitrobenzene and 40 gms. NaOH were sealed in a bomb tube and heated under pressure to 170° C. The contents of the tube after heating for about one half hour were still crystalline but proved to be unchanged p-chloronitrobenzene since it melted at 80°-83° C.

The p-nitroacetanilide used for the preparation of p-nitrophenol was made by Heath and Mulligan. It was necessary to reflux 100 gms. of this product for two days with 75 gms. NaOH in one liter of water in order to obtain the sodium salt of the p-nitrophenol. A yield of 122 gms. which is nearly quantitative, was obtained in the second run from 100 gms of p-nitraniline. The p-nitrophenetol was first made by refluxing the sodium nitrophenolate with alcohol and ethyl bromide. About 200 gms. of the sodium salt of p-nitrophenol were dried at 110° and mixed with one liter of absolute alcohol and 140 gms. of ethyl bromide. The mixture was heated under the reflux condenser for five days. The next run was made by heating the same amount of reagents in an autoclave for four hours. The alcohol was distilled off and recovered. About 200 c.c. of 95% alcohol were obtained. The p-nitrophenetol was steam distilled in both experiments. In the first experiment 140 gms of p-nitrophenetol crystallized from alcohol were obtained. This is a yield of about 75%. With the autoclave only 50 gms of p-nitrophenetol were obtained. Alcohol and some ether were obtained as





side products.

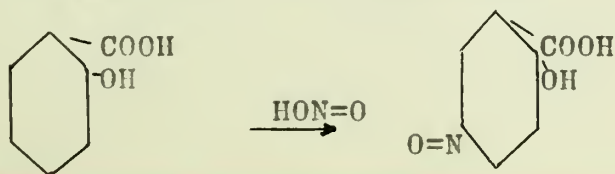
### Conclusion.

In the heating of p-chloronitrobenzene with alkali no results can be obtained by heating under pressure. However, if p-bromonitrobenzene is heated with alkali under reflux for several hours the p-nitrophenol is obtained. Bleaching powder can be used to form p-nitrosophenol hydrochlorite from p-nitrosophenol but this compound cannot be converted into p-nitrophenol by use of sodium hydroxide. The p-nitrophenol can however be prepared almost quantitatively if p-nitro acetanilide is refluxed with sodium hydroxide for several hours. The p-nitrophenetol is prepared from p-nitrophenol by treating the sodium salt of the latter with alcohol and ethyl bromide.

### Part III. Study of the Preparation of Nitrososalicylic Acid.

#### Historical and Theoretical.

This compound is mentioned in a patent by Friedrich Bayer and Co.<sup>8</sup> Friedlander doubts the possibility of the reaction proceeding, although he has not been able to collect any definite data. The work done here shows that the reaction does not proceed. However it was only tried under the usual conditions.





### Experimental.

The procedure was as follows: Exactly 50 c.c. of glacial acetic acid were added to 10 gms. of salicylic acid to which 5 gms. of  $\text{NaNO}_2$  were added. Trials were made by adding the sodium nitrite slowly and rapidly. In every case much heat was evolved accompanied by brown fumes of nitrogen oxides. After allowing the reacting mixture to stand over night the precipitate was filtered and washed with water. The light yellow crystals at first formed turned darker but proved to be unchanged salicylic acid. In the next run 20 gms. of salicylic acid were dissolved in one liter of water and the solution was made neutral with alkali. After adding 12 gms. of sodium nitrite acetic acid was used to make the solution strongly acid. From the dark red colored solution was obtained yellow crystals upon adding  $\text{HCl}$ . The product melted at  $153-60^\circ \text{C}$ . which is the same as salicylic acid. Because the melting point of nitroso salicylic acid is not known, a combustion for nitrogen contents was made. The run showed no percent of nitrogen, which shows that the product was unchanged salicylic acid.

### Conclusion.

Experiments show that the direct treatment with nitrous acid cannot be used for the preparation of nitroso salicylic acid which is only given up to this time as a procedure among the German patents.





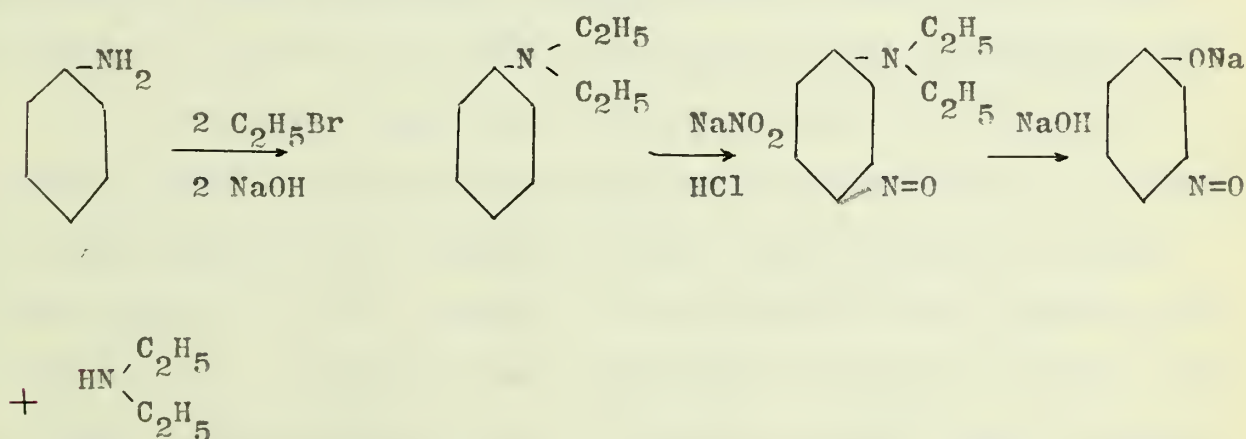
## Part IV. Preparation of Diethylaniline and Diethylamine.

## Historical.

This compound has been prepared by Hofmann<sup>9</sup> with the aim of stopping at the monoethyl derivative and separating it. From there he proceeded to diethylaniline. The para position left free is easily attacked so that this compound reacts easily with other compounds to form stable dye-stuffs. Dimethylaniline is much more important in the dye-stuff industry than the diethyl compound since it can be prepared more readily.

## Theoretical.

An alteration in the process of Hofmann<sup>9</sup> was made and successfully carried out. By this alteration the process was carried out in one step with the diethylaniline as the finished product. The reaction was then carried on to diethylamine but nitrosophenol as a side product was not recovered.





### Experimental.

In the first process 100 gms. of aniline were refluxed with 140 gms. of ethyl bromide for about thirty minutes. Then 30% NaOH was added slowly until 100 c.c. had been added; exactly 140 gms. more of ethyl bromide were added and refluxing continued as 100 c.c. of the NaOH were added. The diethylaniline was then separated and distilled off with a yield of 142 gms. or 90% yield. It was then decided to alter the directions given by Hofmann and proceed to diethylamine. To this end 30 gms. of diethylaniline were added to 120 gms. of concentrated HCl and 150 c.c. of water added. At 0° C. 16 gms. of sodium nitrite in 80 c.c. of water were slowly added. Then 210 c.c. of 30% NaOH were added and the entire volume evaporated to about 50 c.c. To this residue 200 c.c. of 30% NaOH were added and distilled up to 98° C. The distillate was allowed to stand over stick NaOH and redistilled collecting 5 gms. of diethylamine at 55-60° C. The p-nitrosophenol was not recovered. A second run, in which the nitroso-diethylaniline was added slowly to boiling sodium hydroxide solution and the other part of the procedure carried out as before, yielded 12 gms. of diethylamine.

On a somewhat larger scale diethylaniline was prepared as before. About 3.5 pounds were prepared with recovery of 1.5 pounds of ethyl bromide and 4 pounds of NaBr from 4 pounds of aniline and 9 pounds of ethyl bromide. At the same time the autoclave was used. One mole of alcohol was substituted for one of the two moles of ethyl bromide necessary and the mixture heated under pressure. It was found that only the one mole of ethyl bromide had reacted because mono-ethylaniline was formed.



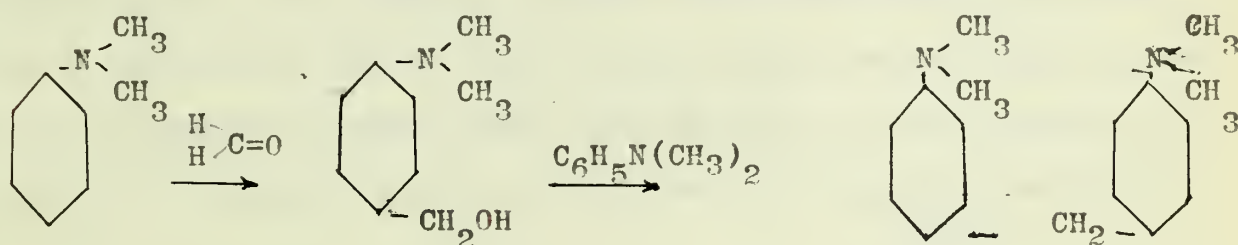
## Conclusion.

It was found that diethylaniline could be prepared on a large scale by allowing plenty of time for the two moles of ethyl bromide to react in the presence of alkali. This process can be carried out in one step. The autoclave offers no advantage.

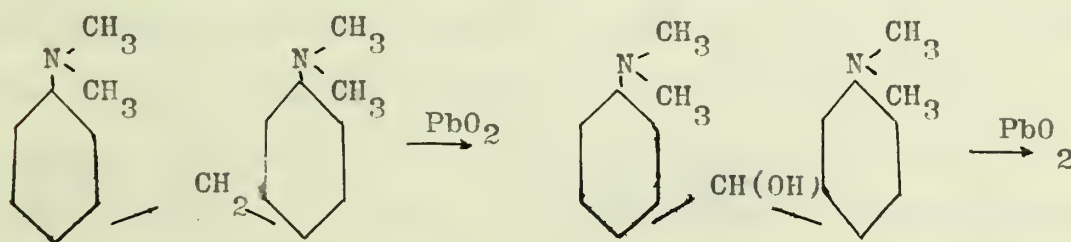
## Part. V. Preparation of Michler's Ketone and Some of its Derivatives.

### Historical and Theoretical.

Möhlau<sup>10</sup> and Michler<sup>11</sup> are used as references here. The first work was the formation of tetramethyldiaminodiphenylmethane according to Möhlau<sup>10</sup>.

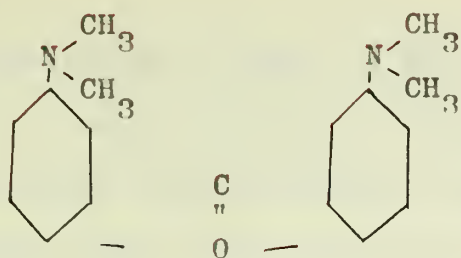


This product is oxidized -Möhlau<sup>10</sup> to the alcohol and it was thought that the same reaction could be carried further to the ketone.

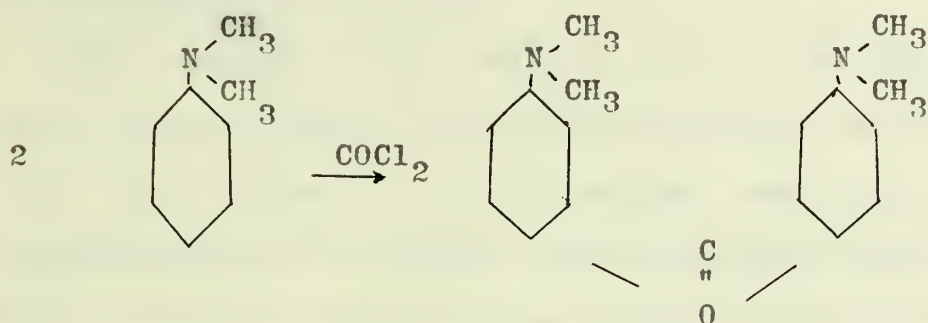








Michler's ketone or tetramethyldiaminobenzophenone has been investigated extensively by Michler.



Michler states that phosgene reacts with dimethylaniline at ordinary temperature but it was found in this work that they do not react at ordinary temperature. Upon heating to  $120^\circ\text{C}$ , nearly one half of the phosgene is lost. More phosgene must then be added.

#### Experimental.

The first work was the preparation of one run of tetramethyldiaminodiphenylmethane according to Mohlau<sup>10</sup>. The next step was the oxidation to the alcohol by means of  $\text{PbO}_2$ . It was thought that twice the amount of  $\text{PbO}_2$  needed to oxidize to the alcohol could be added and with a little heating the ketone could be prepared. Exactly 12.7 gms. of the tetramethyldiaminodiphenylmethane





were dissolved in 10 gms. of HCl (sp. gr. 1.18) and a mixture of 500 c.c. of water and 5 c.c. glacial acetic acid with 500 gms. of ice was added. With stirring a paste of 12 gms. of  $\text{PbO}_2$  was added. The mixture which contained the alcohol was allowed to stand until it warmed to room temperature and another 12 gms. of  $\text{PbO}_2$  was added with warming. Upon neutralizing the solution with sodium hydroxide no trace of the ketone was obtained. An intense blue colored dyestuff was present.

It was decided at this point to take up the formation of the ketone by use of phosgene and dimethylaniline. The directions of Michler<sup>11</sup> were followed closely. Phosgene was passed into 120 gms of dimethylaniline at ordinary temperature with shaking until an increase in weight of 25 gms. was obtained. The dimethylaniline in excess was removed by steam distillation. Upon adding sodium hydroxide no ketone was precipitated. The next run was heated on the water bath for two hours after the phosgene was run in but no ketone was obtained. A greyish blue precipitate was formed which melted at  $235^{\circ}\text{C}$ . which Michler claimed to be the ketone. Toluene was used as a solvent for the phosgene but upon refluxing most of the phosgene escaped. The next run was heated for three hours on a steam bath after running in the phosgene. Upon weighing there was a slight loss detected. The mixture was next heated for three hours at  $120-30^{\circ}\text{C}$ . Upon weighing this time nearly one half of the phosgene had escaped. Phosgene was again added and the heating repeated until there was no loss upon heating to  $150^{\circ}\text{C}$ . The procedure was then followed as before. A light brown oily precipitate was obtained which was recrystallized from alcohol. When



acetone was used for a solvent, 7 gms. of pure Michler ketone melting at  $171-2^{\circ}$  was obtained.

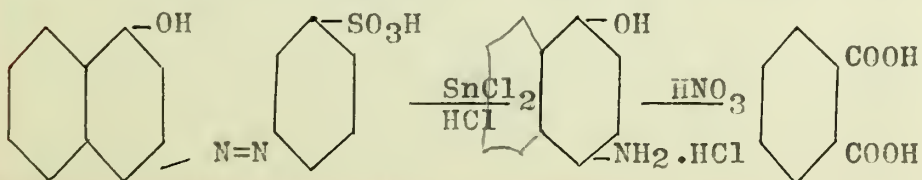
### Conclusion.

Michler's ketone can be prepared if phosgene is added to dimethylaniline until the correct gain in weight has taken place after heating to  $150^{\circ}\text{C}$ . It does not form immediately and at ordinary temperatures as stated by Michler<sup>10</sup>.

### Part VI. Preparation of Phthalic Acid from $\alpha$ -Naphthol Orange.

#### Historical and Theoretical.

Phthalic acid is now being made commercially by oxidation of naphthalene and other derivatives. However some difficulties are experienced apparently since phthalic anhydride is quoted at present at \$5.00 per pound. In the process used here, Liebermann<sup>12</sup> was followed for the preparation of  $\alpha$ -naphthol orange from  $\alpha$ -naphthol and diazo-sulphanilic acid. The hydrochloride of Orange I or amido-naphthol hydrochloride was prepared then by use of  $\text{SnCl}_2$  and  $\text{HCl}$  according to Siedel<sup>13</sup>. This product was broken down with the formation of phthalic acid by oxidation with nitric acid.





### Experimental.

About 12 gms. of amidonaphthol hydrochloride were prepared from 35 gms. of  $\alpha$ -naphthol orange. The next step was the oxidation to phthalic acid with nitric acid. No reference was found for this. The entire yield of 12 gms. of amidonaphthol hydrochloride was heated with 30 c.c. of nitric acid (sp. gr. 1.43) on the water bath for three hours and then cooled. As water was added large crystals were formed. These were recrystallized from water and dissolved in alkali and reprecipitated with acid. A yield of 5 gms. was obtained while the theoretical yield is 11 gms.

### Conclusions.

Phthalic acid can be prepared by the oxidation of 1,4-amidonaphthol hydrochloride with nitric acid. 1,4-Amidonaphthol hydrochloride may readily be prepared by reduction of  $\alpha$ -naphthol orange.







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